

IMPORTANCE OF ACTIVE SITES IN COAL CHAR AND CARBON GASIFICATION

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INTRODUCTION

A fundamental understanding of the kinetics of coal gasification requires the knowledge of the role of (a) carbon active sites, (b) inherently present catalysts and (c) diffusivity of the reactant gases within the pores of the (usually) rapidly devolatilized char (1). The pressing need for design data for the new generations of coal gasification processes probably justifies the great number of essentially empirical kinetic studies that provide useful correlations, but in which the above factors are lumped into overall empirical parameters (e.g., reactivities) which cannot be related to measurable physical properties of the chars. The predictive capabilities of such correlations and the possibility of their extrapolation are uncertain, at best. A parallel effort is needed in order to obtain more fundamental kinetic parameters.

Many coal researchers have not fully realized the relevance, to the kinetics of coal gasification, of studies performed on relatively pure and highly crystalline materials such as graphitized carbon blacks and graphite. A recent comprehensive review by Essenhigh (2) emphasizes the value of these studies in helping to understand coal reactions. The purpose of this paper is to provide experimental evidence for the usefulness (and necessity of application!) of the concept of active sites in understanding the gasification behavior of lignite chars.

EXPERIMENTAL

A North Dakota lignite (3) was pretreated with HCl and HF in order to remove essentially all the inorganic constituents (4). Chars were prepared by both slow and rapid pyrolysis in N₂ (99.99% purity). Slow pyrolysis (10 K/min) was performed in a conventional horizontal-tube furnace at temperatures between 975 and 1475 K and residence (soak) times up to 1 h at final temperature. Rapid pyrolysis (~ 10⁴ K/s) was effected in an entrained-flow reactor (5,6) at 1275 K. The residence time was varied between 0.3 s and 5 min. The reactivity of the various chars and carbons of increasing crystallinity, from Saran char to SP-1 graphite, was determined by isothermal thermogravimetric analysis (TGA) in 0.1 MPa air. Weight changes were recorded continuously as a function of time. The maximum slope of the burn-off vs. time plot (R_{\max}) was used as a measure of gasification reactivity. In a series of preliminary runs, discussed in detail elsewhere (6), appropriate reaction conditions were selected to eliminate interparticle and intraparticle heat and mass transfer limitations. The reported rates are, therefore, thought to be intrinsic, chemically controlled values.

Elemental analyses were performed on the chars in order to determine their C/H ratios and thus the extent of their devolatilization. Physical adsorption of CO₂ at 298 K was measured and micropore volumes were determined using the Dubinin-Radushkevich equation (7). The concentration of carbon active sites (active surface area) was measured by oxygen chemisorption on the chars at 375 K and 0.1 MPa air (6,8).

RESULTS

Table 1 gives the C/H ratio, micropore volume and oxygen chemisorption capacity of the demineralized (Dem) lignite and selected Dem-chars. Unless otherwise noted

Table 1

SELECTED PROPERTIES OF DEMINERALIZED LIGNITE AND CHARs
PRODUCED UNDER DIFFERENT PYROLYSIS CONDITIONS

Sample	C/H (atomic, daf)	Micropore Volume (cm ³ (STP)/g)	Oxygen Chemisorption Capacity (wt% oxygen)
Dem-Coal ^b	1.2	-- ^a	--
R - 0.3 s	3.8	93 ^c	7.2
R - 1.2 s	--	98	5.4
R - 1.8 s	7.2	107	4.3
R - 5 min	13	104	2.3
S - 0 h ^d	5.8	--	--
S - 30 min	--	98	--
S - 1 h	11	--	1.6
S - 1 h (975 K)	--	--	3.4
S - 1 h (1475 K)	--	--	0.72

^a Not determined

^b R = rapid pyrolysis

^c At 298 K (near critical temperature for CO₂) the density of liquid CO₂ is about 1.0 g/cm³. Thus the liquid volume is about 0.2 cm³/g.

^d S = slow pyrolysis

in parentheses, all char samples were prepared at 1275 K. Figure 1 shows the effect of pyrolysis residence time at 1275 K on the subsequent reactivity of the char. Significant char deactivation is observed with increasing pyrolysis severity. A similar effect is observed by increasing the temperature of pyrolysis. Figure 2 shows the Arrhenius plots of reactivity for chars and carbons of increasing purity and crystallinity. The Saran char was prepared by slow pyrolysis of Saran at 1225 K for 3 h.

DISCUSSION

The demineralized lignite can be considered as the most convenient "model compound" for studying the uncatalyzed coal char gasification reactions at a fundamental level. It contains about 2000 ppm of impurities, compared to about 8% in the original lignite. This is still a relatively high level of potential catalysts when compared to carbons of higher purity also used in this study: spectroscopically pure natural graphite (SP-1, Union Carbide Corp.), with < 6 ppm; graphitized carbon black (V3G, Cabot Corp.), with < 120 ppm; Saran char (Dow Chem. Co.) with < 100 ppm. However, most of the remaining inorganics are present in the form of relatively poorly dispersed discrete minerals (such as clays and pyrite) which are not thought to be very efficient in catalyzing char gasification in air (9).

Even though the weight loss during rapid pyrolysis at 1275 K is essentially complete after about 1 s (6), it is seen in Table 1 that the evolution of hydrogen is a relatively slow process. There exists a qualitative correlation between the decrease in char reactivity and the increase in C/H ratio of the chars. It is also seen in Table 1 that the micropore volume of the Dem-chars is relatively high, of the same order of magnitude as for typical carbonaceous adsorbents (~ 0.3 - 0.4 cm³/g). Accordingly, the total surface area is also expected to be high. The oxygen chemisorption capacity, calculated from the amount of CO and CO₂ evolved upon the decomposition of the carbon-oxygen complexes, is seen to decrease by a factor of about ten with increasing severity of pyrolysis.

Table 2 summarizes and integrates the reactivity and surface characterization results. Total surface area (TSA) was calculated using the Polanyi-Dubinin approach (10), by assuming that micropore volume is approximately equal to the monolayer capacity. It is concluded that if this is a measure of the true total surface area, then TSA is not a relevant reactivity parameter. A difference in observed rates (per unit mass) of about five orders of magnitude (column 4) is reduced only by about two orders of magnitude when TSA is taken into account (column 5).

Oxygen chemisorption capacity was transformed into active surface area (ASA) by assuming that each chemisorbed oxygen atom occupies about 0.08 nm^2 (11). The values are given in column 3 of Table 2. Rate constants per unit ASA are given in column 6. It is seen that a difference in observed reactivities of Dem-chars of a factor of twelve is reduced to within a factor of three when expressed on this basis. The value of ASA for the Saran char was obtained under conditions similar to those used in this study. In the case of V3G, chemisorption was effected at 575 K and 65 Pa O_2 , also in the absence of gasification. It is assumed that the value of oxygen content thus obtained is also a measure of ASA. For SP-1 graphite the geometric edge area was taken as ASA. It is seen that differences in observed reactivities of about five orders of magnitude between the most reactive Dem-char and the least reactive SP-1 graphite are reduced to within one order of magnitude when their ASAs are taken into account. The relatively small differences in the rate constants in column 6 are attributed to the effects of catalysis. It is seen that lower values are consistently obtained for chars (carbons) of higher purity. Also, in lignite chars which have been subjected to more severe pyrolysis conditions the dispersion of the inherent catalyst (CaO) was shown to be lower (6). Catalysis is expected to play a greater role in chars which have undergone milder heat treatment. This is, indeed, suggested by the relatively high rate constants of the short-residence-time and low-temperature chars.

CONCLUSIONS

The oxygen chemisorption capacity of demineralized lignite chars at 375 K and 0.1 MPa air gives an indication, at least from a relative standpoint, of the concentration of carbon active sites in them. It certainly provides an index of their gasification reactivity. The commonly observed and heretofore empirically treated coal char deactivation with increasing severity of pyrolysis conditions was thus correlated with a decrease in a measurable fundamental property of the chars: carbon active surface area. The importance of the concept of carbon active sites in gasification reactions was also illustrated for carbons of increasing crystallinity from a Saran char to SP-1 graphite. Total surface area, as estimated by the Polanyi-Dubinin approach, was shown not to be a relevant reactivity parameter.

ACKNOWLEDGEMENTS

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Table 2
SURFACE AREAS AND REACTIVITIES OF DEM-CHARS AND CARBONS
OF INCREASING PURITY AND CRYSTALLINITY

Sample	TSA (m ² /g)	ASA (m ² /g)	R ₇₀₀ (g/g/h)	R ₇₀₀ (g/m ² TSA/h)x10 ³	k ₇₀₀ (g/m ² ASA/h)x10 ³
R - 0.3 s	630	225	1.8	2.9	8.0
R - 1.8 s	730	133	0.94	1.3	7.1
R - 5 min	710	73	0.30	0.42	4.1
S - 30 min	665	-- ^a	0.28	0.42	--
S - 1 h	--	50	0.25	--	5.0
S - 1 h (975 K)	--	108	1.2	--	11
S - 1 h (1475 K)	--	25	0.15	--	6.0
Saran char	1,224 ^b	50 ^b	0.15	0.12	3.0
CB-Monarch 700	206	--	0.05	0.24	--
GCB-V3G	63 ^b	< 1 ^b	-2x10 ⁻⁴ ^c	0.0032	> 0.2
SP-1 graphite	1.8	< 0.1	-2x10 ⁻⁵ ^c	0.011	> 0.2

^aNot determined

^bData taken from Ref. 12

^cExtrapolated value

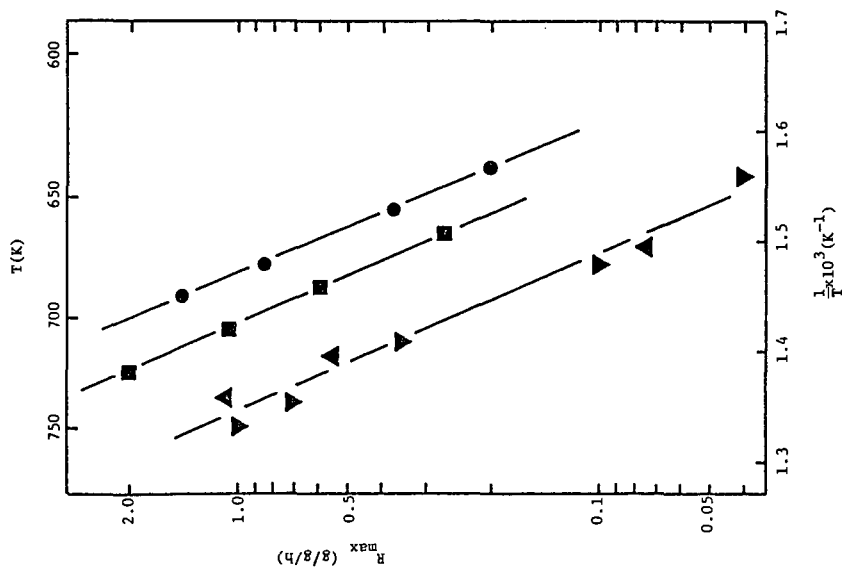


Figure 1

Effect of Pyrolysis Residence Time Between 0.3 s and 1 h on the Reactivity of Den-Char. Pyrolysis Temperature, 1275 K (0.1 MPa Air):

\bullet R - 0.3 s; \blacksquare R - 1.8 s; \blacktriangle R - 5 min; \blacktriangledown S - 1 h

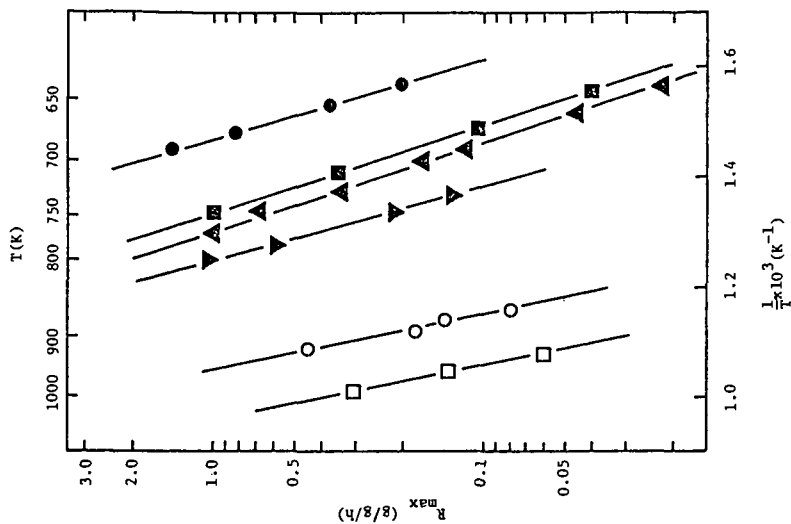


Figure 2

Arrhenius Plots of Reactivity of Chars and Carbons of Varying Degree of Crystallinity and Purity (0.1 MPa Air):

\bullet R - 0.3 s; \blacksquare S - 1 h; \blacktriangle Carbon Black (Monarch 700); \blacktriangledown Graphitized Carbon Black (V3C); \square SP-1 Graphite